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Significant Accomplishments and Conclusions.

In research funded by the ONR Young Investigator Award, our group was the first to investigate electrochemical reactions at solid electrodes of nanoscopic dimensions. The results have implications in redox chemistry of colloids and supported catalysts and in chemical analyses using miniaturized electrodes. Initial work (1) using ultra-thin platinum band electrodes demonstrated a departure of mass-transfer-limited voltammetric currents from predictions based on continuum fluid structure. We proposed an original model that described the dependence of molecular transport on near-surface diffusivity and the dimensions of the reacting electroactive molecule that quantitatively predicts the observed behavior. A detailed theoretical analysis of the effect of the electrical double layer on both electron-transfer kinetics and mass transfer at sub-micron electrode structures was developed that indicates that significant departure from the classical voltammetric waveshape and current magnitude is expected when one of the electrode dimensions is reduced below ~10 nm (11). A new method of synthesizing Pt disk microelectrodes of nanometer dimensions was developed based on using a scanning tunneling microscope (STM) to induce localized dielectric breakdown on TiO_2 coated Pt substrates (16). These electrodes are currently being employed to test theoretical predictions.

In a second area of research, STM was employed to investigate electroactive molecular films (2). The research addressed issues regarding the potential-dependent molecular and electronic structure of adsorbed redox molecules and is motivated by fundamental questions regarding molecular forces that lead to film formation, correlation of molecular structure with electrochemical activity, and charge delocalization in electroactive molecules and polymers. The electrochemical deposition of an organometallic complex, $Re(CO)_3$(v-bpy)Cl, was investigated in one of the first applications of STM for analyzing molecular reactions at surfaces (5). In this study, the molecular structure of electrogenerated adsorbates was correlated with the potential at which deposition was performed. This work has been continued with a recent demonstration that the density of electronic states associated with adsorbed protoporphyrin(IX)FeCl, as measured in tunneling spectroscopy experiments, is in good agreement with predictions from the classical electron-transfer theories. Electron-tunneling rate constants measured between a STM tip and individual molecules are in quantitative agreement with heterogeneous rate constants obtained using conventional electrochemical methods. In a separate study, the heterogenous electron-transfer rate constant for ferrocene oxidation was correlated with the local density of states, as measured using STM (13). The significance of these contributions is reflected by recent invitations to write reviews articles for *Modern Reviews of Physics*, *Analytical Chemistry*, *Comments on Inorganic Chemistry*. and *Chemical Analysis Series* .

Several significant experimental and theoretical contributions to the understanding of interfacial fluid structure were also made during the award period. The first application of the Israelachvili surface forces microbalance to investigate interfacial structure at metal/electrolyte junctions were initiated (14). These studies showed that surface forces can be measured in solutions to within ~ 1 nm of the electrode surface and have set the stage for detailed measurements of the electrical dougle layer. In collaboration with researchers at the Minnesota Supercomputer Institute, a generalized hard-rod free-energy functional density approximation has been developed for the electrical double layer. The theory has been applied to symmetrical and asymmetrical electroytes for various surface charge densities and shown to compare very well with Monte Carlo simulations (7, 9, 10).

Applications of phase-measurement interference microscopy (PMIM) for in-situ topographical imaging of electrode surfaces was developed in a fourth area of research (3, 8). In one application, PMIM was used to image (with 5Å resolution) the nucleation and growth of localized corrosion pits on Fe electrodes immersed in H_2SO_4. The data were analyzed to obtain kinetic rate equations for pit growth.

Personnel

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All technical reports were published in refereed journals.

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